Organization	Oak Ridge National Laboratory
Project Title:	Geochemistry of Aluminum in High Temperature Brines(‘)
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Presenter:	Pascale Bénézeth
FY 1998s and 1999 Funding:	$90 K/year(2)

Project Purpose and FY 1998 and 99 Objectives: The objective of this research is to provide quantitative data on the equilibrium and thermodynamic properties of aluminum minerals required to model changes in permeability and brine chemistry associated with fluid/rock interactions in the recharge, reservoir, and discharge zones of active geothermal systems. This requires a precise knowledge of the thermodynamics and speciation of aluminum in aqueous brines, spanning the temperature and fluid composition ranges encountered in active systems. The empirical and semi-empirical treatments of the solubility/hydrolysis experimental results on single aluminum mineral phases form the basis for the ultimate investigation of the behavior of complex aluminosilicate minerals. The principal objective in FY 1998 was to complete the solubility measurements on boehmite ($AlOOH$) in $NaCl$ media (1.0 and 5.0 molal ionic strength, 100-250°C). However, additional measurements were also made on boehmite solubility in pure $NaOH$ solutions in order to bolster the database for fitting in-house isopiestic data on this system. Preliminary kinetic measurements of the dissolution/precipitation of boehmite was also carried out, although these were also not planned in the earlier objective. The 1999 objectives are to incorporate these treatments into existing codes used by the geothermal industry to predict the chemistry of the reservoirs; these calculations will be tested for reliability against our laboratory results and field observations. Moreover, based on the success of the experimental methods developed in this program, we intend to use our unique high temperature pH measurement capabilities to make kinetic and equilibrium studies of pH-dependent aluminosilicate transformation reactions and other pH-dependent heterogeneous reactions.

FY 1998 and 99 Performance and FY 2000 Plans: During this research program, an analytical method based on ion chromatography was developed to allow concentrations of aluminum at sub-ppb levels to be determined with sufficient accuracy (±10%) to allow measurements to be made at the solubility minima of gibbsite and boehmite, even in saline solutions. This technique, which also involves sample collection and pretreatment procedures, is applicable to sampling natural waters in the field, where contamination and precipitation can lead to misleading and erroneous results.

The treatment of the recently acquired boehmite solubility data in $NaCl$ solutions is complete and now a consistent set of thermodynamic quantities are available for the boehmite dissolution equilibria from 100 to 290°C, and from infinite dilution to five molal ionic strength. Moreover the hydrolysis quotients obtained at these conditions are fully consistent with those derived from gibbsite dissolution and already published from our earlier program. In fact, it was found that there is considerable covariance between the formation constants for $Al(OH)_2^+$ and $Al(OH)_3^o$ values, such that it was necessary to force a linear reciprocal temperature (Kelvin) dependence, including the value at 50°C from the gibbsite data in order to obtain realistic thermodynamic parameters for these two hydrolysis equilibria.

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“‘Represents partial budget of larger program in FY 1998 and 99.

As yet unpublished, isopiestic data on sodium aluminate solutions from 110 to 169°C are available from the work of Howard Holmes (retired) carried out in our laboratory for the geothermal program.
Due to the restricted concentrations of aluminate that could be reached in these solutions, modeling of the resulting osmotic/activity coefficients according to the Pitzer ion-interaction model proved to be ambiguous. The cause of this problem rests with the pure $NaAl(OH)_4$ parameters, which could not be uniquely specified without having data at high mole fractions of this salt. Although solubility data exist in the literature for boehmite in relatively high caustic solutions, it was decided to conduct some batch experiments to verify the accuracy of these results and to provide the needed high aluminate concentrations that would contribute to the modeling effort. A series of experiments was conducted from 100 to 200°C in a Teflon-lined autoclave up to approximately four molal total NaOH, with aluminate concentrations up to 1.9 molal. Beyond this concentration, precipitation of an aluminate phase occurred in the sampling lines dictating the upper concentration limit for these experiments. A preliminary Pitzer model of the $NaAl(OH)_4$ - NaOH system using these results and selected studies taken from the literature is complete. This model is not only consistent with our previously published, low temperature (<80°C) results based on gibbsite solubility experiments, but only required three independent variables (temperature-dependent terms) to fit the ion interaction parameters for the entire system. Two manuscripts describing the thermodynamics of boehmite dissolution are currently in preparation.

By monitoring the change in pH with time, considerable kinetic information can be obtained without the need for sampling. Therefore, studies of the dissolution/precipitation rates of boehmite were initiated in neutral to basic solutions at 100 to 290°C at 0.1 molal ionic strength. In FY 2000, the dissolution/precipitation kinetics and solubilities of aluminosilicates will be studied with the intent of addressing problems associated with brine reinjection, scaling, and corrosion in down-hole and in-plant systems. Studies will involve equilibrium solubility and dissolution/precipitation rate determinations of gibbsite at low temperature (50-70°C), and for a number of aluminosilicate phases prevalent in geothermal reservoirs at higher temperatures, using the hydrogen-electrode concentration cell. The principal limiting factor in the use of these cells will be the formation of additional phases during the course of the experiments. Therefore, we will first initiate studies of gibbsite, for which equilibrium data are available from earlier work in this program and we know that at least in the case of the dissolution reaction, no other phases are formed. We will then undertake to investigate aluminosilicate solubility equilibria and kinetics by first determining the dissolution and precipitation kinetics of increasingly complex aluminosilicates, such as kaolinite, dickite and feldspars. Natural kaolinite from Decazeville, France, is already available and will be used after treatment to remove traces of iron oxide.

The hydrogen-electrode concentration cell approach is also entirely amenable to studies of the rates and equilibrium constants of mineral transformation reactions, such as the hydrolysis of feldspars via reactions such as the alteration of potassium feldspar to muscovite and quartz:

$$3KAlSi_3O_8 + 2H^+ \rightleftharpoons KAl_3Si_3O_{10}(OH)_2 + 2K^+ + 6SiO_2$$

If these phases react sufficiently rapidly to achieve equilibrium in a few weeks at temperatures of 200-300°C in our cells, which are magnetically stirred with high efficiency promoting rapid attainment of solid/liquid equilibrium, the kinetics will be investigated in detail. This knowledge will aid in predicting pH, steam corrosivity and scale formation in geothermal systems. Furthermore, by first establishing an equilibrium K^+/H^+ ratio, then quickly changing this ratio by titration of acid, base, or potassium into a solution in equilibrium with the mineral assemblage, and monitoring pH to a new equilibrium value, we can obtain the rates of reaction, both at near- and far-from-equilibrium conditions, as a function of temperature, pH, salinity, and mineral grain size. This will enable us to test commonly used fluid geothermometers, determine the pH imposed by various mineral assemblages on circulating brines, and help lay the framework for realistic fluid/rock interaction rate models.

FY 1998 and 99 Results: During FY 1998 and 1999, the final experiments were performed to complete the study of the solubility of boehmite from 100 to 290°C in brines at concentrations from 0.03 to 5 molal. These final experiments involved four sets of solutions at 1 and 5 molal (NaCl). For two sets the batch sampling mode was used as the pH was controlled with excess HCl, so that the dominant aluminum species in solution was Al^{3+}. The remaining experiments were performed in dilute NaOH where the aluminate anion predominates and it was therefore necessary to measure the pH *in situ* with the ORNL's unique hydrogen-electrode concentration cell. The previous boehmite work focused on measuring the pH dependence of the solubility isothermally, mainly at lower ionic strengths. Each isothermal set of resulting "pH profiles", which in some cases comprised up to five individual experiments, has now been treated to yield the solubility quotients, Q_{sn} (n=0-4), corresponding to the reaction: $AlOOH_{(s)} + (3-n)H^+ \rightleftharpoons Al(OH)_n^{3-n} + (2-n)H_2O$. These quotients, together with those alluded to above for the end-member species and selected values from the literature, have each been fitted as functions of temperature and ionic strength, including the appropriate Debye-Hückel terms. Two manuscripts describing these results and the experimental approach are being prepared. Moreover, these functions have been used to generate new parameters for the Chiller and EQ3/6 commercial programs and these are now being tested against our most recent data.

As an example, Figure 1 represents the logarithm of the solubility quotients for the reactions:

$$AlOOH + 3H^+ \rightleftharpoons Al^{3+} + 2H_2O \qquad Q_{s0}$$
$$AlOOH + 2H_2O \rightleftharpoons Al(OH)_4^- + H^+ \qquad Q_{s4}$$

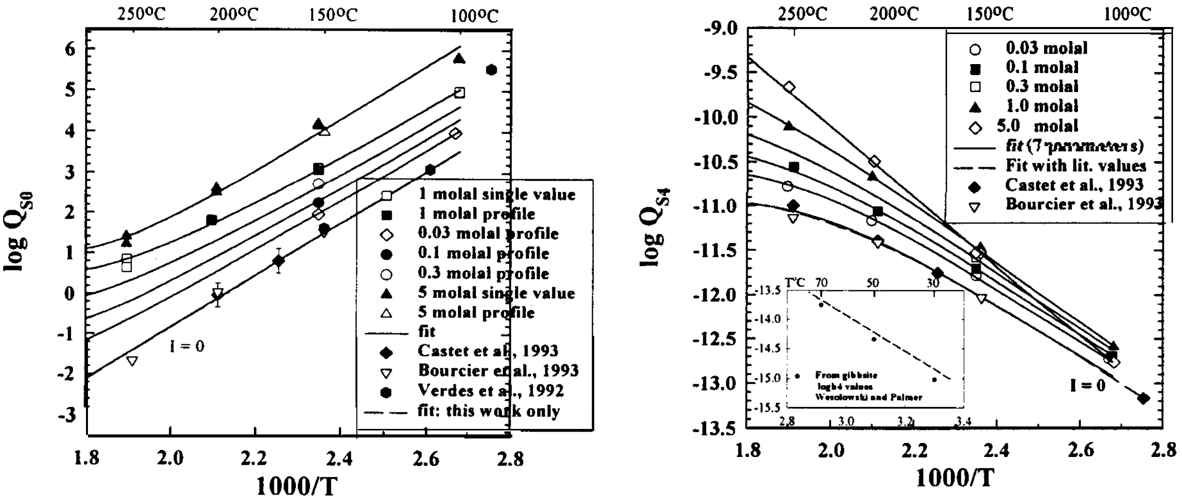

Figure 1

obtained in the present study as a function of reciprocal of temperature, at different ionic strengths, and compared with the literature values at infinite dilution.

Note that one solubility experiment was performed involving gibbsite in contact with an acidic saline solution (I=0.03 molal) in the hydrogen-electrode concentration cell at 70°C. The solubility quotient, Q_{S0}, obtained under these conditions was found to be in exact agreement with that obtained by the laborious batch method (Palmer and Wesolowski, 1992) using a different source of purified gibbsite. This is not only very reassuring in terms of the intrinsic reliability of the results obtained in this research program, but also opens the door for future kinetic studies on gibbsite with this unique technique.

A logical extension of the solubility studies on boehmite in NaCl brines was to conduct a number of solubility studies in tetramethylammonium chloride (TMACl) solutions in moderately basic solutions at 200°C (I = 0.1 molal). The large, singly-charged TMA’ cation is known to form very weak ion pairs with singly-charged aqueous anions. We therefore attempted to use this approach to determine the extent of ion pairing between the aluminate anion $Al(OH)_4^-$ and Na’, by titration of a NaCl/NaOH solution into the hydrogen-electrode concentration cell. Recent literature studies provide conflicting ion pair association constants for this interaction. However, we were unable to detect any increase in solubility with increasing sodium concentration and can therefore only place a possible maximum value on this constant at this time. We have successfully completed the first stage of the modeling program for the $NaAl(OH)_4 - NaOH$ system. The modeling effort is based on the Pitzer ion interaction treatment, incorporating the osmotic coefficient data (1 IO- 169°C) from Howard Holmes (retired, ORNL) and equilibrium solubility quotients for the reaction:

$$AlOOH + OH^- + H_2O \rightleftharpoons Al(OH)_4$$

These quotients were either obtained in the current geothermal program late last year (a limited number of experiments at 100, 150 and 200°C), or found in the literature as summarized by Apps, Neil and Jun, NUREG/CR-5271. The tabulated results in this report refer to solubility experiments by Magarshak (1938), Fulda and Ginsberg (1951), Russell et al. (1955), Bemshtein and Matsenok (1961), and Kuyunko et al. (1983). The β^0, β^1, β^2, and C parameters for pure aqueous NaOH were supplied as a subroutine based on expressions from Simonson, Mesmer and Rogers (1989). The expression for $\beta^2(NaAl(OH)_4)$ was taken directly from its relationship to the ion-pair association constant, which was taken from SUPCRT92 with parameters supplied by Prokovskii and Helgeson (1995). This constant proved to give a superior fit to the data compared to that derived from the ion pair constant reported by Diakonov et al. (1996). The values of β^0, β^1, C for $(NaAl(OH)_4)$, as well as the mixing parameters $\theta_{OH.Al(OH)4}$ and $\psi_{Na,OH,Al(OH)4}$, were fixed at 25°C according to Wesolowski (1992), which were based on the equivalent gibbsite solubility data. The infinite dilution solubility constants were taken from our boehmite solubility data. It was found that the only three temperature-dependent terms were needed to fit the entire boehmite solubility/osmotic coefficient data set from 100 to 250°C. The temperature-dependent terms were in the parameters β^0 and β^1 for $NaAl(OH)_4$, and $\psi_{Na.OH.Al(OH)4}$. A number of data points were then excluded from the fit, including all the results of Fulda and Ginsberg (195 1), in order to obtain the optimum fit factor.

We have also adapted the commercial code EQ3/6 database formulated on the Pitzer model to include the parameters of Wesolowski (1992) for sodium aluminate and NaOH from Simonson, Mesmer and Rogers (1989). This modification allows the code to run to 300°C, even given the limited temperature dependence for sodium aluminate recommended by Wesolowski. These parameters will next be replaced by the parameters derived from the present work. However, the current predictions of the modified EQ3/6 program to 300°C also tend to confirm that only small modifications are needed (i.e., as indicated by the need for only three temperature-dependent adjustable variables), in order to fit the high temperature solubility data, which in turn supports the overall conclusion that we now have a unified model for aqueous aluminum from ambient to high temperature, and from infinite dilution to solutions with ionic strengths on the order of 20 molal.

The rates of both boehmite dissolution and precipitation reactions are extremely fast at high pH, so that only the runs performed at 100°C have been analyzed in detail to extract the kinetics of these processes. However, the equilibrium solubilities obtained after each addition of acid or base (see arrows in Figure 2 as an example at 152.4°C) were in excellent agreement with our previous solubility measurements (solid lines in Figures 2 and 3) performed at the same conditions as can be seen in Figure 3.

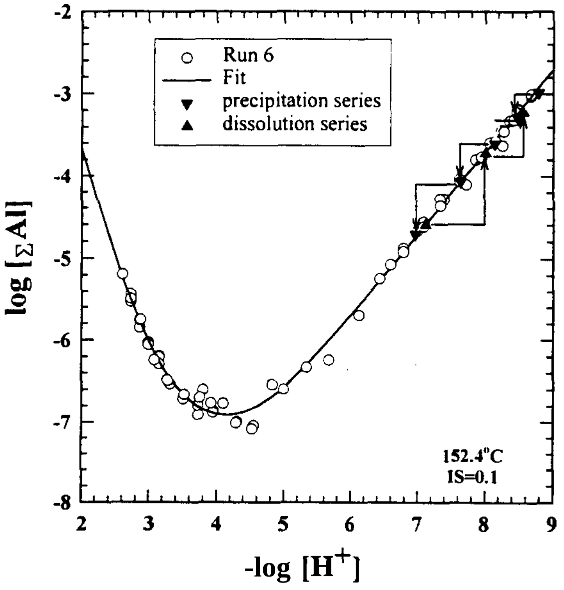

Figure 2

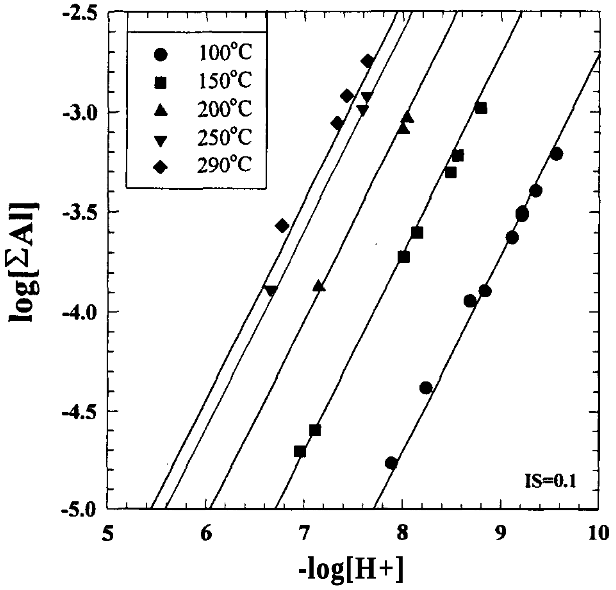

Figure 3

The rate of dissolution of boehmite was first converted from pH_m versus time to total aluminum molality $[Al(OH)_4^-]$ versus time based on the known stoichiometry of the reaction. Both plots followed an exponential dependence with time as equilibrium was approached. Applying "the principle of detailed balancing", the dissolution reaction, which was monitored following a small addition of base, seems to obey the following simple rate law:

$$d[Al(OH)_4^-]/dt = k_{diss}C - k_{prec}\,Cm_{H+}m_{Al(OH)4-}$$

where C stands for the ratio of total surface area of boehmite to the mass of solution, k_{diss} and k_{prec} are the zero-order and second-order rate constants for dissolution and precipitation, respectively, and m_x represents the appropriate molal concentrations. Thus plots of rate, $d[Al(OH)_4^-]/dt$, versus $[H^+][Al(OH)_4^-]$ were linear with an intercept and slope proportional to the respective rate constants. Comparison of the rate constants extracted from these plots showed good agreement. The ratio of the forward and reverse rate constants should be equal to the overall solubility quotient. For the two dissolution cases investigated, the ratios were in excellent agreement, within 0.1 log units, with the corresponding equilibrium constants determined previously for the boehmite reaction on the basic side. The same simple rate law should be applicable to the precipitation reaction steps (i.e., those generated by the addition of acidic titrant), assuming that no other metastable phase is first formed on the surface of the boehmite crystals. The precipitation steps are currently being analyzed.

Technology Integration: A consistent set of thermodynamic parameters generated in this program define the prevalent aqueous aluminum species, as well as the chemical composition of solutions in equilibrium with rock-forming minerals, at geothermal reservoir conditions. The results are being treated to allow them to be readily incorporated into chemical reaction and transport computer codes in common use by the geothermal industry. We have been in contact with Dr. Mark Reed (Department of Geological Sciences, University of Oregon) who has provided us with a number of databases (Soltherm) for the program Chiller, which we have tested against our most recent results. Moreover, we have had contact with Dr. Thomas Wolery (LLNL) concerning the EQ3-6 database (data0) and are currently making modifications to it in order that it be consistent with our experimental results. We had direct contact with Dr. Darrel Gallup (Unocal Corp.) concerning problems associated with collection and storage of field samples for aluminum analysis. In general, the dissolution/precipitation kinetics and solubilities of aluminosilicates will be studied with the intent of addressing problems associated with brine reinjection, scaling, and corrosion in down-hole and in-plant systems.

Acknowledgments

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